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Understanding Germanium Coordination and Raman Signatures in GEO_2 Glass Using First Principle Molecular Dynamics

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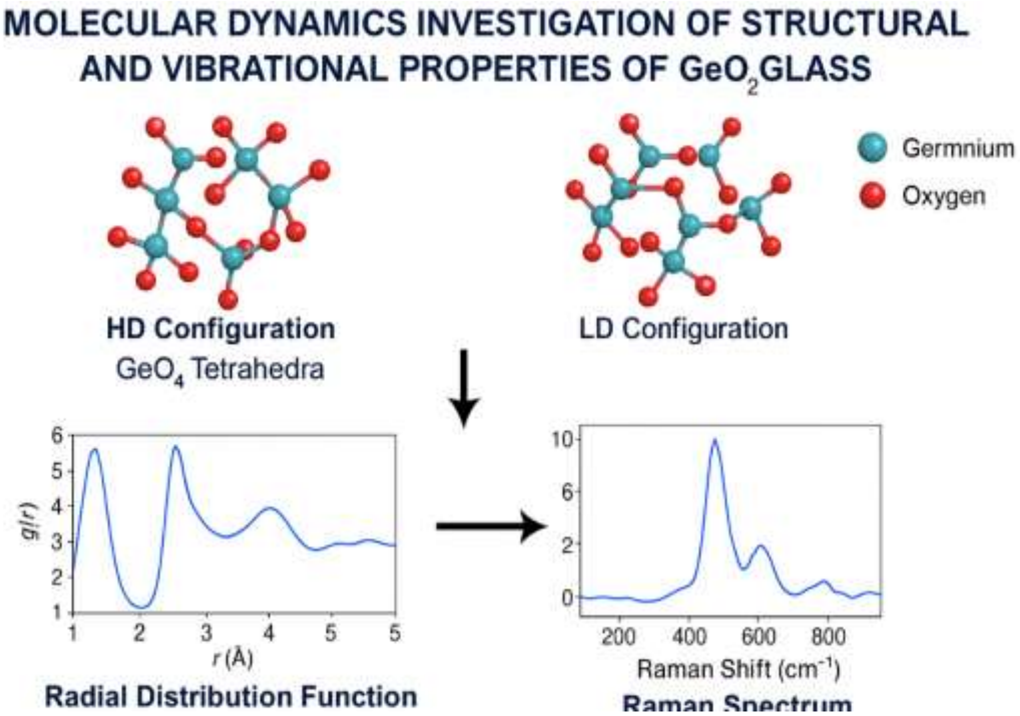
Abstract

Research on infrared material production focuses on GeO_2-based glasses because of their excellent optical transmission combined with exceptional mechanical strength and thermal stability properties. The oxide glass formulation offers increased manufacturing benefits and extended design possibilities compared to crystalline ceramics because it requires lower production costs. Pure plane wave ab initio molecular dynamics methods support the researchers in studying structural and vibrational characteristics of GeO_2 glass. The research characterizes germanium coordination patterns and separates two major organizational designs which comprise GeO_4 tetrahedral arrangements called high-density (HD) and low-density (LD). Short- and intermediate-range order characteristics emerge from analyzing bond distances together with bond angles and radial distribution functions (RDFs). The results derived from analyzing Raman spectral features of vibrational density of states (VDOS) show accurate matches with declared experimental findings. Our findings prove that atomic level motion strongly relates to the macroscopic properties of vibrational behavior needed for designing future infrared and photonic systems involving GeO_2 materials.

Keywords: GeO_2 glass, Raman spectroscopy, molecular dynamics simulation, optical design, pure plane wave.

Graphical Abstract



Introduction

The development of advanced photonics and optoelectronics as expanded research for IR-transparent materials which must demonstrate high mechanical properties alongside excellent optical properties and thermal behavior. The excellent optical properties of crystalline ceramics come at the cost of high processing difficulty and expensive production. In contrast, oxide glasses—particularly germanium dioxide (GeO_2)—offer versatile and cost-effective alternatives with promising infrared transmission properties (Nalam, 2023)s,(Al Mahalawy et al., 2021).

The atomic-scale examination and structural properties of GeO_2 glass remains limited even though chalcogenide and halide glasses have gained increased attention for infrared technological applications (Boolchand, 2000). The local and intermediate-range order of GeO_2 glass demands detailed investigation because it enables property enhancement necessary for optical communications and modulators and thermal imaging systems applications.

The atomic-scale phenomena can be effectively observed with first-principles based molecular dynamics (MD) simulations (Ootani et al., 2020). This research implements ab initio molecular dynamics using plane wave basis to study GeO_2 glass structures and vibrational characteristics. Such methods allow researchers to study germanium coordination structures together with medium-range ordering phenomena and the fundamental vibrational modes appearing in Raman spectra.

Methodology

A GeO_2 glass model was developed using *ab initio* molecular dynamics within the density functional theory (DFT) framework(Marchin & Du, 2024), as applied in the Vienna Ab initio Simulation Package (VASP). Electron interactions were treated using projector augmented-wave (PAW) potentials incorporated with the Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation (GGA). A plane wave cutoff energy of 500 eV was used to ensure computational accuracy.

In generating an amorphous configuration, a melt-quench process was applied: the system was balanced at 3000 K, then gradually cooled to 300 K at a rate of 10 K/ps within the NVT ensemble using a Nosé–Hoover thermostat. Structural relaxations were executed on the final configuration prior to analysis of its structural and vibrational properties.

Results and Discussion:

Structural Analysis

The simulations revealed that germanium atoms originally adopt tetrahedral coordination (GeO_4 units), most especially in the high-density (HD) phase. On the other hand, the low-density (LD) phase exhibited distorted tetrahedral structure. The Radial distribution functions (RDFs) showed a prominent Ge–O peak near 1.74 Å, consistent with neutron diffraction results (Ghigna et al., 2002). Bond angle distributions were centered around 109.5°, characteristic of tetrahedral geometry, although the LD phase exhibited broader distributions indicative of structural disorder.

Coordination and Medium-Range Ordering

Germanium atoms exhibited an average coordination number of ~4.0 in the HD phase, but this differ between 3.5 and 4.2 in LD regions, portraying the dynamic flexibility of the Ge–O network. Medium-range order analysis—using ring statistics and partial structure factors—revealed the prevalence of 6-membered rings, further supporting the glass network's topological diversity.

Vibrational and Raman Spectral Features

Vibrational analysis was carried out via the vibrational density of states (VDOS), allowing recognition of key vibrational modes. Characteristic features, including Ge–O symmetric stretching and bending vibrations, were found to have strong agreement with experimental Raman spectra(Zhang et al., 2022). Remarkably, vibrational modes exhibited shifts between HD and LD regions, highlighting the sensitivity of vibrational properties to local structure(Baiz et al., 2020).

Applications and Implications

These findings gave an essential insights into the atomic-scale dynamics of GeO_2 glass, simplifying rational tuning of its properties through compositional or processing adjustments. Applications benefiting from this work include IR-transmitting optics, waveguides, optical switches, and thermal imaging systems, where control over vibrational behavior directly impacts device performance.

Conclusion

This study presents a comprehensive molecular dynamics investigation of GeO_2 glass, revealing critical details of germanium coordination, structural motifs, and vibrational properties. The use of a pure plane wave *ab initio* approach enables accurate modeling of both local and intermediate-range order, providing strong connection with experimental Raman spectra. These insights contribute to a deeper understanding of IR-transparent oxide glasses and support the development of advanced materials for future photonic technologies.

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